SPECIFIC CONTRIBUTIONS OF SIMS AND XPS TO STUDIES OF THERMAL OXIDE FILM

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SPECIFIC CONTRIBUTIONS OF SIMS AND XPS TO STUDIES OF THERMAL OXIDE FILMS

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Résumé - Le SIMS donne des informations spécifiques sur la diffusion d'un traceur dans un film d'oxyde en cours de croissance et sur la distribution d'impuretés en faibles concentrations dans le film. L'état de valence de ces dopants peut être déterminé par XPS, permettant ainsi d'expliciter leur influence sur les processus de diffusion.

Abstract - SIMS give specific informations on the diffusion of a tracer in growing oxide films and the depth distribution of impurities in low concentrations in the films. The valency of these dopants can be determined by XPS, thus permitting to explain their influence on diffusion processes.

The oxidation resistance of metallic alloys is determined by the growth kinetics of the oxide film and its adherence. These macroscopic properties are easily characterized by thermogravimetry and mechanical tests. But diffusion kinetics deduced from thermogravimetry data differ sensibly from the prediction of models, even in the case of pure single phased oxide films. The classical theory proposed for the growth of such films is based on the diffusion of atoms under the control of unidirectional stoechiometry gradients from the outer surface to the oxide-substrate interface, with diffusion coefficients measured in pure oxides at equilibrium. It does not take into account the complex structure of growing oxide films, resulting from interfacial stresses (interface with the substrate and between oxide grains) : lattice deformations changing the activation energy of diffusion, anisotropic cristallisation, dislocation networks, intergranular voids and cracks, all constituting short path for diffusion.

Thus analytical technics such as Secondary Ion Mass Spectrometry or Nuclear Reaction Analysis, permitting to determine diffusion profiles of marked isotropes in thin layers, are very useful to study the diffusion processes in thermal oxide films.

On the other hand, metallic materials always contain impurities and deliberate additions, which dissolve or precipitate in the oxide film and drasticaly modify all its structural, mechanical and physicochemical properties. It is thus important for the optimisation of the composition of heat-resisting alloys, to characterize :

- the depth distribution of impurities in the film. The SIMS technique is perfectly suited for this purpose, because of its high sensibility,

- their eventual segregation along grain boundaries or their precipitation. The STEM is the most performant technique in this field, but ionic microscopy can also provide interesting results, avoiding the problem of making thin a film without changing its structure,

- the valence state of these foreign atoms and their influence on the electronic structure of the host lattice, which determines the concentration of point defects in the crystal and their mobility. X ray Photoelection Spectroscopy give partial but easily accessible informations concerning this topic. However there are very few data on the insertion sites and valence states of dopants in oxides ; for instance, no data are available for important impurities such as C, S, Si.

Examples were choosen to illustrate the complementarity of specific informations obtained by SIMS and XPS.

More detailed data on the oxidation mechanism of the studied materials are given elsewhere (1 to 4). The used machines were a CAMECA SMI 300 microscope (5) and a LEYBOLD LMS 10 equipment (6). Particular conditions of experiments are given in figure captions.

I - DIFFUSION PROCESSES IN PURE NiO, Cr_2O_3 FILMS

The experimental procedure used in our experiments with ^{18}O involved oxidizing the samples successively 24 h in natural oxygen, then 24 h in an atmosphere enriched with 25% ^{18}O and finaly 60 h in natural oxygen again, in order to obtain films of comparable thicknesses during the three cycles. Other cycling sequences based on the parabolic law of oxide growth might have been used. When the oxygen diffusion is negligeable, the ^{18}O profile would have a square wave form (curve A of figure 1), slightly distorded by the rugosity of interfaces (curve B). The importance of oxygen diffusion may be deduced from the unsymmetry of profiles and from the $^{18}O/(^{16}O+^{18}O)$ ratio in the enriched layer.

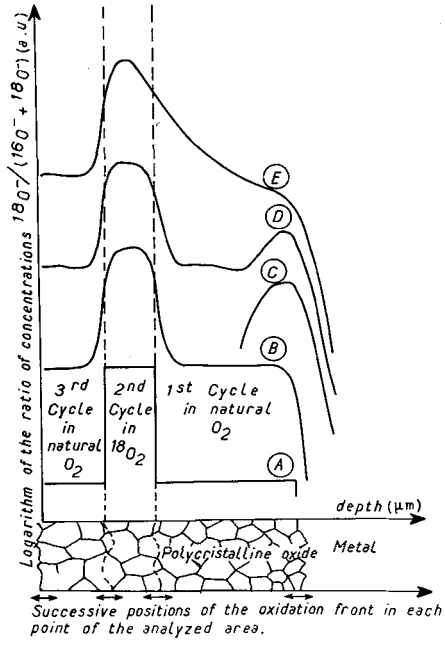

Fig. 1 - SIMS profiles of the depth distribution of an ^{18}O tracer in oxide films (5.5 keV Ar^+ bombardment under residual vacuum) :

A) theoretical profile resulting from the cyclic modifications of the atmosphere composition

B) theoretical distorsion of this profile by rugosities of interfaces

C) contribution of the tracer diffusion along short circuits in NiO films

D) experimental profile in a NiO film 7 µm thick formed on Ni oxidizes 108 h at 620°C

E) experimental profile in a Cr_2O_3 film 5 µm thick formed on 63Ni/37Cr oxidized 108 h at 800°C.

In the case of NiO film (curve D), the apparent width of interfaces on profiles (corresponding to a decrease from 90% to 10% of the ^{18}O or ^{16}O emissions) corresponds exactly to their average rugosities measured by talystep. The relative thicknesses of oxide formed during the three successive cycles are in good agreement with thermogravimetry data (1). The symmetry of the profile and the $^{18}O/(^{16}O+^{18}O)$ ratio in the enriched layer indicate that cationic diffusion is largely preponderant in the bulk of the oxide. A second maximum of ^{18}O is often observed at the metal-oxide interface (curve C) for samples oxidized at low temperatures (600°-800°C). It was attributed to a diffusion of the tracer in short circuits, thus permitting to explain that the diffusion kinetics have a low activation energy in this range of temperature (1).

In the case of pure chromia films developed on a 63Ni/37Cr alloy (curve E), evidence of the diffusion of the tracer can be detected on the profiles. However the diffusion of cations is more important than that of oxygen.

II - INFLUENCE OF IMPURITIES ON THE OXIDATION OF Ni

Si, Al, S, C, alkalines and alkaline earths are traditional impurities of Ni grades ; they may also be introduced at the surface during polishing or thermal treatments.

We observed for instance that the oxidation kinetics of pure Ni (containing less than 50 ppm impurities in the bulk) varies of a factor 3 according to the polishing mode of the surface. This fact was connected with the important modifications of the surface rugosity, of the film cristallisation according to the strains in the Ni surfaces and of impurities introduced in the film (MORVAN J., PIVIN J.C., ROQUES-CARMES C., submitted for publication in Acta. Met.).

SIMS profiles of figure 2 show for example that various amounts of Si, Al, K enter in the oxide film according to the polishing mode. In all cases these elements tend to precipitate near the metal-oxide interface. For surfaces annealed or polished electrolyticaly (unstrained surfaces) the growth kinetics of the film is very heterogeneous on different grains of the substrate : the variations in the thickness of the film (and in its color) are connected with variations of a factor 10 in the Si, Al, K concentrations.

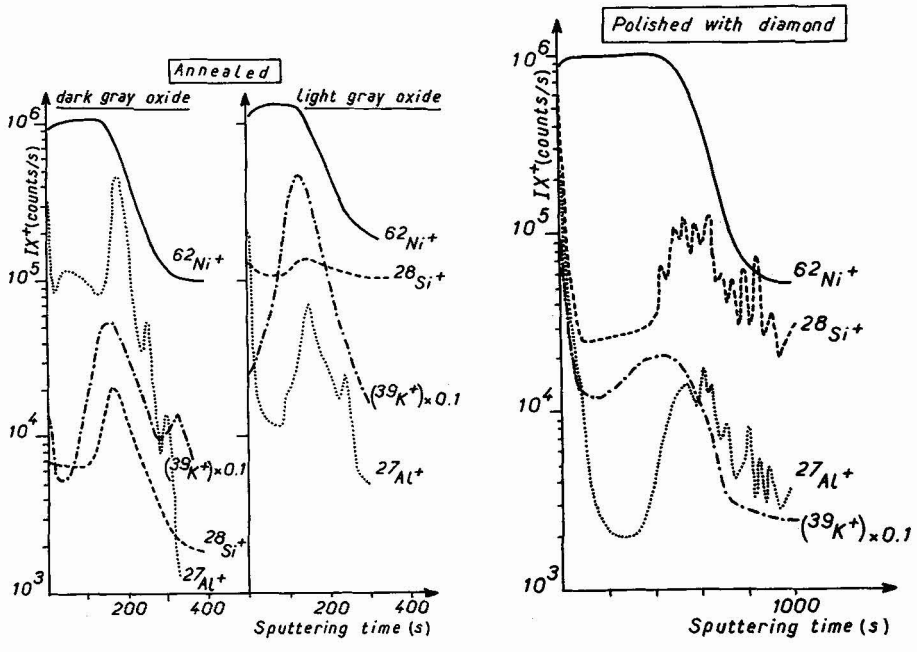

Fig. 2 - SIMS profiles of the depth distribution of some impurities in NiO films formed during an oxidation of 15 mn at 900°C in pure O_2 on Ni samples previously annealed at 1200°C in vacuum, or annealed then polished with 1 µm diamond paste. The profiles were recorded with a 5.5 kev Ar^+ bombardment under residual vacuum ; the analysed area (60 µm in diameter) was smaller than a grain of the substrate.

Experiments on Ni surfaces selectively implanted with S, C, Si (1) have shown that S, Si tend to reduce the oxidation kinetics, while surfaces implanted with C oxidise faster. Neither the ^{18}O diffusion nor the oxide film structure are affected by these implanted impurities (1). Internal stresses in the oxide are sensibly modified by S, Si and less affected by C (2).

The valence of these impurities was determined by X.P.S. on NiO films doped with 0.5% to 2% of C, S or Si on a thickness of a few tens nm by ion implantation (Table 1 and Fig. 3). The comparison of spectra recorded a) on as implanted surfaces, b) on sputtered ones, c) after annealing at 500°C in UHV, d) after exposition to oxygen of sputtered surfaces, have shown that the results concerning the valence of the dopants are not affected by the defects induced by ion irradiation (such as the partial reduction of NiO during sputtering (7).

The results indicate that C, S, Si atoms are inserted in the lattice on Ni sites or intersticial sites as C^{2+}, S^{2+} and Si^{4+} respectively. In all cases this would account for the formation of additional Ni vacancies, accelerating the Ni diffusion in the film. The correlation with the modification of the oxidation kinetics is correct for C, but the effect of S, Si on the electric equilibrium of the crystal must be minor. The modification of the tensor of internal stresses has an opposite and stronger effect.

III - INFLUENCE OF AN Y ADDITION ON THE OXIDATION OF Ni-Cr ALLOYS

Y is added in most heat-resisting alloys developing chromia or alumina films, in order to reduce the growth kinetics of these films and promote their adherence. We could demonstrate with SIMS and ionic microscopy that these beneficial effects are due to the dissolution of a few 100 ppm Y in the film, rather than to a mechanical keying of the film by internal particles of Y_2O_3 (3, 4). On the contrary protuding pegs of Y_2O_3 formed in alloys containing too large concentrations of Y promote the spalling of the film (4).

It was supposed that Y atoms are inserted in the lattice on Cr sites as Y^{3+}. They would associate one or several Cr vacancies in order to suppress the distorsion of the lattice induced by their large size (35% over that of Cr^{3+} ions). SIMS profiles of ^{18}O in the films and XPS study of the electronic structure of the oxide doped with 5% Y give some confirmations of these hypothesis :

- the diffusion of oxygen is preponderant in Cr_2O_3 doped with Y contrarily to pure Cr_2O_3 (see Fig. 1 and 4). The diffusion fluxes of Cr and O become comparable and ^{18}O is distributed throughout the film,
- the valence of Y is 3+ (see Table 1),
- the core levels of O, Cr atoms are not modified, but a shoulder is observed on the O2s peak towards higher binding energies (Fig. 5) indicating that O atoms are more hightly bond. Note also that the peak of uncoupled d electrons decreases because the amount of Cr^{3+} ions with a $(3d)^3$ configuration decreases, while the amount of Y^{3+} ions with a $(4d)^0$ $(5s)^0$ configuration increases (Fig. 5).

The suppression of the oxidation kinetics seems to be only due to a decrease of the Cr diffusion ; the O diffusion becomes preponderant despite the stronger bonds exchanged by these atoms with Y neighbours.

TABLE 1

SAMPLE	BINDING ENERGIES (eV)					BONDS (8 to 12)
	O1s*	Cr 2p 3/2	Ni 2p 3/2	DOPANT LEVEL	DOPANT ENERGY	
NiO + 10^{16} C 100 keV	530.1 531.8		854.7	C 1s	285.0 (288.7) (283.5)	Ni-O C-O (C=O, C-C)
NiO + 2.10^{16} S 100 keV	530.1		855.0	S 2p 3/2	161.5	Ni-O, S-O
NiO + 10^{16} Si 100 keV	530.1		854.3	Si 2s	153.3	Ni-O, $Si-O_2$
NiO + 10^{16} Y 100 keV	530.1		854.5	Y 3d 5/2	156.7	Ni-O, Y_2-O_3
Pure NiO	530.1		854.3			Ni-O
Cr_2O_3 + 10^{16} C 100 keV	530.7	577.1		C 1s	284.5	Cr_2-O_3, C-O
Cr_2O_3 + 2.10^{16} S 100 keV	530.7	577.0		S 2p 3/2	161.7	Cr_2-O_3, S-O
Cr_2O_3 + 10^{16} Si 100 keV	530.7	576.8		Si 2s	153.6	Cr_2-O_3, $Si-O_2$
Cr_2O_3 + 10^{16} Y 100 keV	530.7	576.9		Y 3d 5/2	156.8	Cr_2-O_3, Y_2-O_3
Pure Cr_2O_3	530.7	576.8				Cr_2-O_3

* Slight shifts of binding energies (0.1 to 0.6 eV) due to charges accumulations were corrected by referencing all energies to the known O1s levels in NiO, Cr_2O_3.

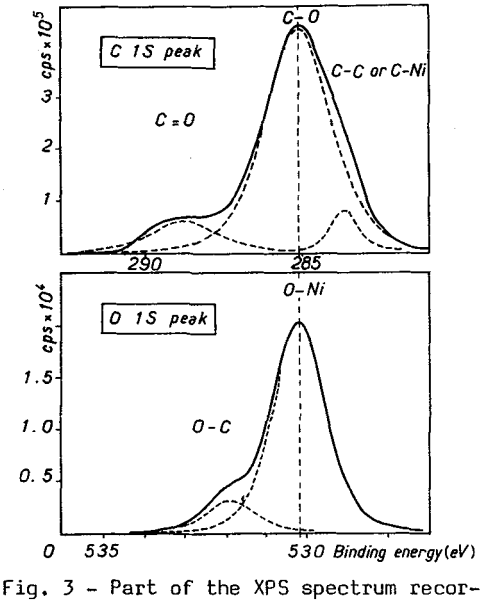

Fig. 3 - Part of the XPS spectrum recorded on NiO implanted with 10^{16} C/cm^2 of E = 100 keV, after removal of 80 nm by sputtering with Ar^+ ions. Conditions of XPS analysis were : Mg Kα radiation, constant pass energy of 50 eV, recording time of 1000 s.

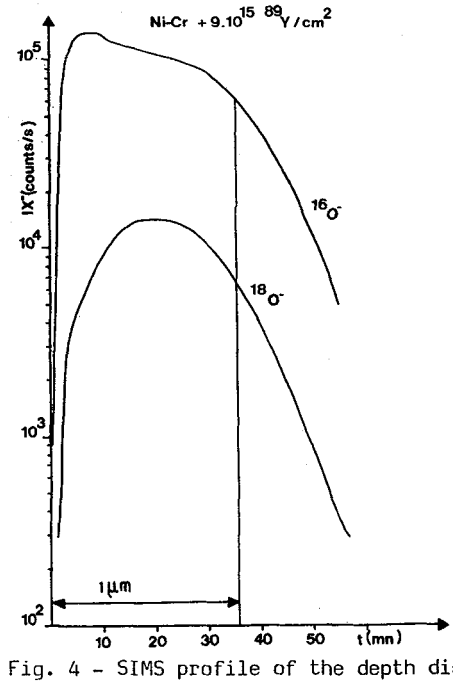

Fig. 4 - SIMS profile of the depth distribution of an ^{18}O tracer in the Cr_2O_3 film formed at 800°C on 63Ni/37Cr doped with 9.10^{15} Y/cm^2 of 100 keV. The Y concentration in the film is about 300 ppm (3).

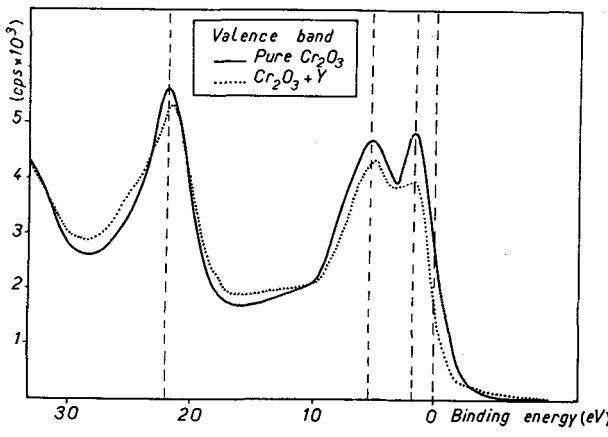

Fig. 5 - Part of the XPS spectrum recorded on Cr_2O_3 doped with 10^{16} Y/cm^2 of E = 100 keV, after sputtering 30 nm. The conditions of analysis are the same as for Fig. 3. The differences in the intensities of O2s peaks (at 22 eV), O2p peak (at 5.3 eV) is due to a difference in the analysed areas. Their slight shift of 0.1 eV is due to a difference in charge accumulation. The peak at 2.2 eV is relative to uncoupled Cr3d electrons.

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